

CYCLIC OLEFINS AS NEW HYDROGEN DONOR COMPOUNDS
FOR COAL LIQUEFACTION

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ABSTRACT

A new set of hydrogen donor compounds, cyclic olefins (CLO), has been evaluated to determine their effectiveness as hydrogen donors to coal. These cyclic olefins are hydroaromatic species which do not contain aromatic rings. The efficacy of these donors has been compared to conventional hydroaromatics. The CLO's under study are 1,4,5,8-tetrahydronaphthalene, also known as isotetralin, and 1,4,5,8,9,10-hexahydroanthracene. CLO's are much more reactive than their conventional hydroaromatic analogues, both in model reactivity studies and in reactions with Western Kentucky No. 9 coal. In this paper, the thermal and catalytic reactivity of the CLO's under nitrogen and hydrogen at coal liquefaction temperature is discussed. Results for the reactions of the CLO's and their conventional hydroaromatic analogues, e.g. tetralin, 9,10-dihydroanthracene, and octahydroanthracene, with Western Kentucky No. 9 coal are discussed.

INTRODUCTION

In both thermal and catalytic coal liquefaction reactions, hydrogen transfer reactions are important avenues by which hydrogen is transferred to coal and substantially increases the amount of coal conversion and upgrading. Hydrogen donors typically used are hydroaromatic and phenolic compounds (1-6). A new set of hydrogen donor compounds has been discovered that are much more effective than conventional hydroaromatics in transferring hydrogen to coal. These donors are cyclic olefins (i.e. hydroaromatic species which do not contain aromatic rings). An example is isotetralin, 1,4,5,8-tetrahydronaphthalene.

The efficiency of isotetralin for converting coal to THF solubles has been shown to be much higher than its conventional hydroaromatic analogue, tetralin (1). In reactions with Western Kentucky No. 9/14 coal, isotetralin converted 80.6% of the coal to THF solubles compared to only 58% for tetralin. This dramatic increase in coal conversion with isotetralin leads to the current investigation of cyclic olefins as hydrogen donors for coal liquefaction.

The objective of this research is to test cyclic olefins as donors for coal liquefaction. The cyclic olefins under study are 1,4,5,8,9,10-hexahydroanthracene (HHA) and 1,4,5,8-tetrahydronaphthalene, isotetralin (ISO). The first step in fulfilling this objective was to investigate the chemistry of these compounds. Both the thermal and catalytic reactivity under hydrogen and nitrogen atmospheres has been determined. The catalysts used were presulfided, pulverized $\text{NiMo}/\text{Al}_2\text{O}_3$ and $\text{Mo}/\text{Al}_2\text{O}_3$. Secondly, these compounds were thermally reacted with Western Kentucky No. 9 coal under a nitrogen atmosphere to evaluate their hydrogen donability.

EXPERIMENTAL

The reactivity and stability of the cyclic olefins were tested in a stainless steel tubing bomb reactor with a volume of 20 cc under the following conditions: 380°C, horizontal agitation at 425 cpm, 1250 psig nitrogen or hydrogen pressure at ambient temperature, reaction times ranging from 15 minutes to 1 hour, 2.0 g hexadecane as the diluent solvent, 3 weight percent CLO, and for catalytic reactions a total active metal loading of 3000 ppm. Two catalysts were used, Shell 324, NiMo/Al₂O₃, and Amocat 1B, Mo/Al₂O₃, to evaluate the catalytic reactivity of ISO at liquefaction conditions. Each catalyst was presulfided, pulverized, and sized between 100 and 200 mesh before being used.

The reactions of both CLO's and three conventional hydroaromatic donor compounds with Western Kentucky No. 9 were also performed. For this study the following reaction conditions were employed: 30 minute reaction time, 1250 psig nitrogen atmosphere at ambient temperature, 380°C reaction temperature, 2.0 g coal, 4.0 g total solvent mixture including 0.1-0.5 weight percent donable hydrogen of the model compound with the balance being fluorene as a diluent solvent, 700 cpm vertical agitation rate, stainless steel tubing bomb reactor of approximately 50 cm³ volume.

The chemicals used were obtained from the following manufacturers and used as received: tetralin, 1,4,5,8,9,10-hexahydroanthracene, 1,2,3,4,5,6,7,8-octahydroanthracene, and 9,10-dihydroanthracene from Aldrich Chemical Co.; 1,4,5,8-tetrahydronaphthalene from Wiley Organics Inc.; Western Kentucky No. 9 coal from PSU/DOE sample bank.

For this work coal conversion is defined as

$$\text{conversion} = 1 - [\text{IOM (maf)} / \text{coal charge (maf)}] \times 100$$

In order to use this definition of coal conversion, both the moisture and ash contents were needed. The moisture content was $4.5 \pm 0.6\%$ and the ash $10.16 \pm 0.14\%$.

RESULTS AND DISCUSSION

ISOTETRALIN SYSTEM

In the model reactivity studies, ISO was very reactive at the catalytic conditions studied; none was observed in the reaction products even at reaction times as short as 15 minutes. Two different presulfided hydrogenation catalysts were used: Shell 324, NiMo/Al₂O₃, and Amocat 1B, Mo/Al₂O₃. These catalysts were chosen because of their different hydrogenation activities with NiMo/Al₂O₃ usually being more active. With ISO in the presence of NiMo/Al₂O₃ and a hydrogen atmosphere, tetralin (TET) was produced as a major product, while no measurable amount of naphthalene (NAP) was formed. With increasing reaction times, less TET was produced, while more decalin (DEC) was formed. With the NiMo/Al₂O₃ catalyst, the trans to cis isomer ratio was approximately 3 to 1. The DEC isomer ratio was independent of reaction time, within experimental error. With Mo/Al₂O₃, the predominant product formed was TET; cis and trans DEC as well as NAP was also formed, yielding approximately 20 weight percent DEC and one weight percent NAP. The trans to cis DEC isomer ratio was approximately 2.5 to 1 and was constant for reaction times ranging from 15 minutes to 1 hour. For ISO, NiMo/Al₂O₃ was a more active hydrogenation catalyst than Mo/Al₂O₃, as evidenced by the greater amounts of DEC produced. The product slate was independent of time, within experimental error, for the reactions performed with the Mo/Al₂O₃ catalyst under equivalent

conditions but varying reaction times; i.e. all the products were formed within the first 15 minutes yielding the same product slate regardless of reaction time.

The thermal reactivity study of ISO showed that all ISO was converted at reaction times of 15, 30, and 60 minutes. The product slate for the thermal reactions differed from that of the catalytic reactions. 1,2-dihydronaphthalene (1,2-DHN) and 1,4-dihydronaphthalene (1,4-DHN) were formed thermally, whereas catalytically they were not. In a nitrogen atmosphere, the predominant product was NAP, with other major products being 1,2-DHN 1,4-DHN, and a minor amount of TET. Approximately 55 weight percent NAP and 40 weight percent DHN's were produced. In a hydrogen atmosphere, the observed products were TET, 1,2-DHN, 1,4-DHN, and NAP. The product slate for the thermal reactions was time dependent. Although the same products were observed, different amounts of each were formed at different reaction times. With increasing reaction time, the amount of NAP produced increased while the amount of 1,2-DHN and 1,4-DHN decreased. The 1,2-DHN to 1,4-DHN isomer ratio varied widely with varying reaction times. At a reaction time of one hour, the 1,4-DHN produced was unexpectedly small; it is believed that 1,4-DHN was rehydrogenated to TET, which would account for the increased TET produced at this reaction time.

HEXAHYDROANTHRACENE SYSTEM

The thermal and catalytic reactivity of 1,4,5,8,9,10-hexahydroanthracene, (HHA) was also examined. As in the ISO reactions, NiMo/Al₂O₃ was a more active hydrogenation catalyst than Mo/Al₂O₃ in the HHA reaction system. With NiMo/Al₂O₃, the predominant products from HHA hydrogenation were isomers of fully hydrogenated anthracene, perhydroanthracene (PHA); the other major products were isomers of octahydroanthracene (OHA) with a minor amount of tetrahydroanthracene isomers (THA) observed. Increasing reaction times favored the formation of the more hydrogenated product PHA, while decreasing the amount of OHA produced. For all reaction times, HHA was totally converted, with either NiMo/Al₂O₃ or Mo/Al₂O₃. With the Mo/Al₂O₃ catalyst, the predominant product was OHA; other products in lesser amounts were PHA and THA. Increasing reaction times increased the amount of hydrogenated product formation. Both OHA and PHA production increased, while that of THA decreased.

In the thermal reaction system for HHA, under both nitrogen and hydrogen atmospheres, the predominant products were isomers of dihydroanthracene (DHA) with 9,10-dihydroanthracene being the major isomer observed. Lesser products included THA and anthracene (ANT). In a nitrogen atmosphere, a trace amount of HHA was observed at the end of the 30 minute reaction time. In a hydrogen atmosphere, with increasing reaction times, HHA recovery decreased. DHA formation decreased, while ANT and THA formation increased. After 60 minutes of reaction in a hydrogen atmospheres, a minor amount of OHA was formed.

COMPARISON OF CYCLIC OLEFINS AND CONVENTIONAL DONORS

The reactivity of the conventional hydrogen donor analogues, DHA, OHA, and TET were compared to that of HHA and ISO under equivalent reaction conditions.

With NiMo/Al₂O₃ in a hydrogen atmosphere, ISO completely reacted, whereas, approximately 25% of TET remained unconverted. The products formed from ISO were TET and DEC, while those from TET were primarily DEC. However, it should be noted that the trans to cis DEC isomer ratio was the same for both compounds, (3 to 1), within experimental error, and that neither ISO nor TET formed NAP as product.

This suggests that ISO was converted to TET by some pathway before forming the more hydrogenated products. With $\text{Mo}/\text{Al}_2\text{O}_3$ in a hydrogen atmosphere, ISO was also completely reacted, whereas, TET remained almost 95% unconverted. However, as was the case with $\text{NiMo}/\text{Al}_2\text{O}_3$, the trans to cis DEC isomer ratio was the same for both ISO and TET (2.5 to 1), within experimental error. This result also suggests that ISO was converted to TET prior to forming DEC.

In thermal reactions, ISO completely reacted under both nitrogen and hydrogen atmospheres. By contrast, TET reacted only slightly in nitrogen producing NAP and was less than 4% converted in a hydrogen atmosphere, forming 1,2-DHN and 1,4-DHN.

The reactions of DHA, OHA, and HHA with $\text{NiMo}/\text{Al}_2\text{O}_3$ in a hydrogen atmosphere produced hydrogenated anthracenes as the predominant products. All three reactants formed PHA, OHA, and THA. DHA and HHA were completely converted to hydrogenated products, whereas OHA remained approximately 32% unconverted. With the $\text{Mo}/\text{Al}_2\text{O}_3$ catalyst, HHA was completely converted, approximately 8% of the DHA remained unreacted, and 98% of the OHA remained unreacted. These comparisons show that catalytically, HHA was much more reactive than either of the conventional hydrogen donor compounds, DHA or OHA.

A comparison of the thermal reactions of HHA, OHA, and DHA showed that in a nitrogen atmosphere HHA completely reacted, the predominant product from HHA hydrogenation being DHA, with lesser amounts of THA and ANT being formed. By contrast, OHA did not react and DHA remained 95% unconverted, with ANT being the only product. In a hydrogen atmosphere more than 98% of HHA was converted, with the predominant product again being DHA. By comparison OHA did not react and only 8% of DHA was converted to dehydrogenated products. The results from the thermal reactions show that HHA was much more reactive than either OHA or DHA at 380°C under both hydrogen and nitrogen atmospheres.

To summarize, when ISO is compared to TET, it is important to note that both thermally, under nitrogen and hydrogen, as well as catalytically, ISO completely converted. By comparison TET did not react thermally, only converted 5% with $\text{Mo}/\text{Al}_2\text{O}_3$ and converted 75% with $\text{NiMo}/\text{Al}_2\text{O}_3$. The comparison of the conventional analogues to HHA showed that DHA was only converted 10% in a thermal reaction system, converted 100% with $\text{NiMo}/\text{Al}_2\text{O}_3$, and converted 90% with $\text{Mo}/\text{Al}_2\text{O}_3$. In a thermal system, under both nitrogen and hydrogen, OHA did not react; with the $\text{NiMo}/\text{Al}_2\text{O}_3$ catalyst, OHA was 68% reacted, while with the $\text{Mo}/\text{Al}_2\text{O}_3$ only 2% converted. HHA was completely converted by both $\text{NiMo}/\text{Al}_2\text{O}_3$ and $\text{Mo}/\text{Al}_2\text{O}_3$. In a thermal system under nitrogen, HHA was completely reacted and was more than 90% converted under hydrogen. Thus, ISO was more reactive than TET, and HHA was more reactive than either DHA or OHA.

REACTIONS WITH WESTERN KENTUCKY NO. 9 COAL

A series of thermal reactions using ISO, HHA, TET, OHA, and DHA with Western Kentucky No. 9 coal in a nitrogen atmosphere was performed. The results for coal conversion to tetrahydrofuran solubles (THFS) is presented in Table I. Each datapoint represented in Table I is the result of at least a duplicate analysis. These are two important aspects to this table. The first is the ranking of the five donor species at the equivalent loading of 0.5 weight percent donable hydrogen. The second is the comparison of HHA and OHA at three different levels of donable hydrogen, 0.5, 0.2, 0.1 weight percent. Important to note in the rankings of the donor species at 0.5 weight percent, is that the two cyclic olefins, HHA and ISO, yielded greater coal conversions than did their conventional

hydroaromatic analogues, TET, OHA or DHA. HHA produced an increase in coal conversion of approximately 12% over its nearest analogue DHA. HHA also showed more than 13% greater conversion than did OHA. ISO yielded approximately 14% greater conversion than did its conventional analogue, TET. All of these comparisons were made on an equivalent amount of donable hydrogen.

When the level of donable hydrogen was varied, HHA consistently converted more than did OHA, albeit, in decreasing differential amounts as the level of donable hydrogen decreased. This result implies that a deficiency of donable hydrogen occurred at these lower levels of donable hydrogen.

For each of the reactions, the THFS fraction was then further analyzed to determine the effect of the coal reaction on the amount of the model hydrogen donor compound that was present in the reaction products. Important to note from this analysis is that for a given hydrogen donor compound, as the level of donable hydrogen was decreased, the products shifted to less hydrogenated species.

A plot of coal conversion versus net grams of H donated from the hydrogen donor is represented in Figure 1. These values were obtained in the following manner. Net grams of hydrogen released (grams of H donated from model compound) - (grams of H going to form other hydrogen donor species). For these calculations, the only other H donor formed was OHA. The solid line shown is the linear best fit to all the data points. The general trend is that as coal conversion increased, the amount of hydrogen donated also increased.

SUMMARY

As seen in both the model compound reactions as well as reactions with Western Kentucky No. 9 coal, the new hydrogen donor compound, cyclic olefins, HHA and ISO, are much more reactive at model liquefaction conditions than either DHA, OHA, or TET. In the model compound reactivity studies, ISO was more reactive, both thermally and catalytically, than TET; HHA was more reactive, both thermally and catalytically, than either DHA or OHA. In reactions with Western Kentucky No. 9 coal in a nitrogen atmosphere, HHA produced an increase in coal conversion to THF solubles of greater than 12% compared to that obtained with OHA, and 12% greater conversion than that obtained with DHA. ISO produced an increase in coal conversion of approximately 14% more than obtained with TET.

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Table I. Coal Conversion Summary for Western Kentucky No. 9

Donor Compound	Conversion* at		
	<u>.5wt% DH</u>	<u>.2wt% DH</u>	<u>.1wt% DH</u>
HHA	88.6(0.04)	78.2(0.5)	64.2(2.5)
ISO	81.0(0.9)		
DHA	76.6(0.8)	73.8(1.1)	62.5(1.2)
OHA	75.5(0.7)	70.2(2.7)	60.3(0.7)
TET	66.8(0.9)		
none	57.4(2.3)	57.4(2.3)	57.4(2.3)

* conversion defined as $1 - \frac{IOM(maf)}{coal(maf)}$
and DH refers to donable hydrogen

**All reactions at 380°C, 1250 psig (cold) N₂ atmospheres, 700 cpm, and 30 minute reaction time.

In the pairs of numbers above, the first is the conversion obtained. The second, in parenthesis, is the standard deviation for that data point.

Figure 1. COAL CONVERSION VERSUS HYDROGEN DONATED.
THREE LEVELS OF DONABLE HYDROGEN,
(0.5, 0.2, and 0.1 weight percent)

